



Effect of FeCl_3 on the photocatalytic processes initiated by UVA and vis light in the presence of TiO_2 –P25



Ewa Adamek^a, Wojciech Baran^{a,*}, Andrzej Sobczak^b

^a School of Pharmacy with the Division of Laboratory Medicine in Sosnowiec, Medical University of Silesia, Department of General and Analytical Chemistry, Jagiellońska 4, 41-200 Sosnowiec, Poland

^b Institute of Occupational Medicine and Environmental Health, Kościelna 13, 41-200 Sosnowiec, Poland

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ABSTRACT

The addition of Fe^{3+} salts to a TiO_2 suspension is one of the methods used to extend the useful radiation range in photocatalytic processes. The aim of this study was to determine how the presence of FeCl_3 affects the photocatalytic reaction mechanism and TiO_2 activity under UVA and vis irradiation.

The photocatalytic degradation of eleven sulfonamides was investigated in the presence of a TiO_2 –P25 suspension, FeCl_3 and a $\text{TiO}_2/\text{FeCl}_3$ mixture.

The addition of FeCl_3 decreased the TiO_2 activity under vis light irradiation but the photocatalytic degradation rate of sulfonamides improved significantly under UVA irradiation. For example, the initial photodegradation rate of sulfisoxazole increased approximately 85 times. The processes carried out in the $\text{TiO}_2/\text{FeCl}_3$ mixture were less sensitive to the presence of free radical scavengers, and the photocatalytic reaction rates were directly proportional to the concentrations of cationic form of the substrates. This result indicates that the photocatalytic degradation rate of the sulfonamides depends on the possibility for direct oxidation of the cationic form of the substrate and its interaction with the catalyst particles via labile electrostatic interactions.

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1. Introduction

An environmental cleaning technology using photocatalytic processes is one of the approaches that allows for the practical use of solar energy. Regardless of their toxicity and resistance to biodegradation, many types of pollutants can be effectively degraded by photocatalytic processes initiated by sunlight [1,2]. Titania (TiO_2) is one of the commonly used heterogeneous photocatalysts for these processes. Unfortunately, the main challenge associated with the widespread use of photocatalysis is the low quantum yield and absence of photocatalytic activity at a wavelength (λ) >400 nm [2–4].

Many published reports have been studied the increase in the TiO_2 photoactivity [1–5]. One of the investigated methods involves extending the useful radiation range to the visible light region [3–8], which can be achieved by modifying the TiO_2 structure by doping with non-metals (i.e., nitrogen, sulfur, fluorine, boron and

carbon), platinoids or lanthanides. However, these methods are not always effective and may increase the overall cost of catalyst production [9].

An increase in the photocatalytic TiO_2 activity was observed in solutions containing Fe^{3+} salts [10–21]. This effect may be due to the intensification of substrate sorption onto the catalyst surface [15–17,20], photochemical synergy of TiO_2 and $\text{Fe}(\text{OH})^{2+}$ ions [10–12,15,18], involvement of Fe^{3+} ions in the redox processes initiated by light or extending the useful radiation range [8–15]. However, Chen et al. [22] determined that Fe^{3+} ions decrease the photocatalytic activity of TiO_2 under visible light.

Fig. 1 shows the most likely mechanism for the processes carried out in the presence of a $\text{TiO}_2/\text{Fe}^{3+}$ mixture under irradiation elaborated on the literature data [10–21].

The aim of this study was to determine:

- how the Fe^{3+} ions affect the TiO_2 photoactivity under UVA and vis irradiation and
- the substrate properties affect the photocatalytic degradation rate.

* Corresponding author. Tel.: +48 0323641562.
E-mail address: bw-xxl@wp.pl (W. Baran).

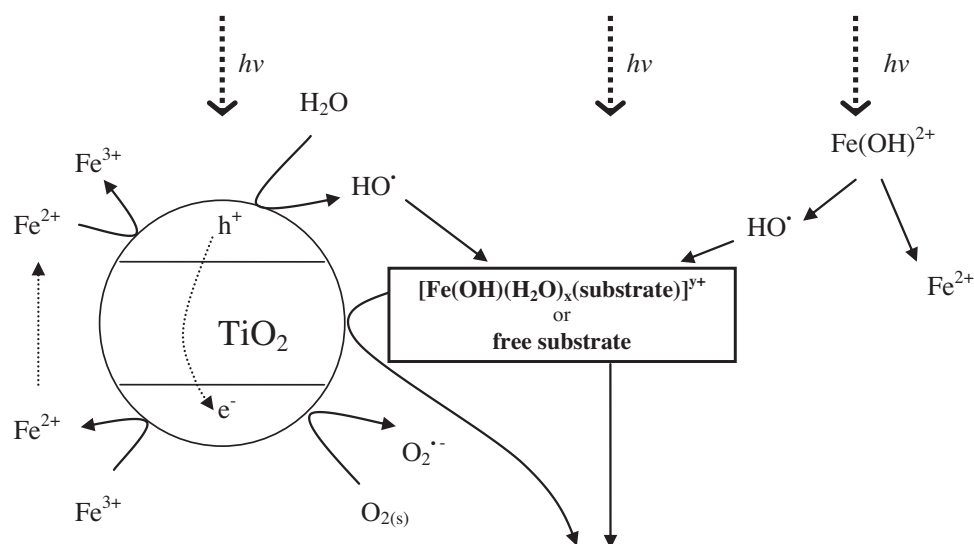
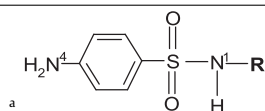


Fig. 1. Photodegradation mechanisms of the organic substrate in the presence of the $\text{TiO}_2/\text{Fe}^{3+}$ mixture based on literature data.

Table 1
Characteristics of the studied sulfonamides.

Name/CAS	Acronym	$-\text{R}^a$	pK_{a1}^b	pK_{a2}^b	Predicted charges for carbon atoms (N^1-R^c)	Polarizability (\AA^3) ^d
Sulfanilamide 63-74-1	SAD	$-\text{H}$	2.46 ± 0.12	10.35 ± 0.21	–	16.25
Sulfacetamide 144-80-9	SCT	$-\text{COCH}_3$	1.96 ± 0.28	5.42 ± 0.31	+0.7453	20.49
Sulfathiazole 72-14-0	STZ		2.22 ± 0.27	7.15 ± 0.12	+0.3781	23.96
Sulfisoxazole 127-69-5	SSZ		1.69 ± 0.27	5.0 ± 0.0	+0.1400	26.93
Sulfamethoxazole 723-46-6	SMX		1.86 ± 0.32	5.73 ± 0.20	+0.4338	24.99
Sulfamethizole 144-82-1	SFZ		2.01 ± 0.14	5.36 ± 0.08	+0.3781	26.26
Sulfadiazine 68-35-9	SDZ		2.15 ± 0.20	6.41 ± 0.14	+0.7200	24.39
Sulfamerazine 127-79-7	SMR		2.21 ± 0.15	6.92 ± 0.14	+0.7200	26.51
Sulfamethazine 57-68-1	SDM		2.40 ± 0.18	7.56 ± 0.26	+0.7200	28.80
Sulfapyridine 144-83-2	SPY		2.69 ± 0.08	8.42 ± 0.14	+0.6863	24.97
Sulfadimethoxine 122-11-2	SDT		2.14 ± 0.44	6.16 ± 0.29	+0.4100	29.60



^a $\text{SH}_2^+ \xrightleftharpoons{k_{a1}} \text{SH} \xrightleftharpoons{k_{a2}} \text{S}^-$, the sources are given in the Supplementary material.

^c The source – ChemBio 3D Ultra 2014 software, MMFF94 method.

^d The source – DrugBank database.

Table 2
Characteristics of the radiation sources

Radiation sources	Abbr.in text	Manufacturer	I (W m ⁻²) in the wavelength range		
			<315 nm	315–400 nm	400–1050 nm
Four fluorescent lamps (Actinic BL TL40 W/10)	UVa lamps	Philips	<0.02 ^a	13.6	6.0
Four fluorescent lamps (Pro TL-D 90 De Luxe 18 W/950)	Vis lamps	Philips	~0 ^a	0.22	43.0

^a Based on the manufacturer's data.

2. Materials and methods

2.1. Reagents

Sulfanilamide and its derivatives were used as model reagents. All of the sulfonamides (SNs) used in the experiments were analytical grade (>98% purity) and manufactured by Sigma–Aldrich. The characteristics of the SNs are listed in Table 1. All of the SN solutions (0.1 mmol l⁻¹) used in the experiments were prepared in redistilled water.

Solid TiO₂ (Aeroxide® TiO₂-P25, Evonik-Degussa GmbH, Germany) and FeCl₃ (pure for analysis, POCH Gliwice, Poland) were employed as components of the photocatalytic system. HCOOH and CH₃CN (pure for HPLC) were used as components of the mobile phases and purchased from POCH Gliwice.

2.2. Adsorption

Solid TiO₂ (0.05 g) and/or 1 ml of the FeCl₃ stock solution (0.1 mol l⁻¹) were added to each SN solution (100 ml). The pH of these samples (solution and suspensions) was adjusted to 3.0 with a concentrated HCl solution (<0.1 ml). Then, the mixtures were magnetically stirred in the dark for 30 min followed by centrifugation (30 min, 4000 RPM). The supernatants were analyzed using HPLC. After the addition of TiO₂ or FeCl₃, all of the operations were carried out in the dark at 20 °C.

2.3. Acidic hydrolysis

Concentrated HCl was added to the SN solutions, and the final concentrations of HCl were 0.1 mol l⁻¹. These samples were placed in closed flasks in a water bath shaker (type 357, Elpan, Poland) for 21 days at 40 °C. Aliquots were periodically removed at 24 h intervals and analyzed by HPLC. In addition, the initial SN solutions at their original pH (without addition of HCl) were stored for 21 days at 40 °C and used as reference solutions. The experiment was carried out under sterile conditions.

2.4. Irradiation

The sample preparation procedure was the same as that described in Section 2.2. These mixtures were magnetically stirred in the dark for 30 min prior to irradiation. Next, open glass crystallizers (500 ml, exposed surface: 102 cm²) containing each prepared mixture were irradiated using UVa or vis lamps (Table 2). The irradiation intensity (*I*) was measured by a quantum-photo radiometer Delta Ohm DO 9721 (Italy). In the experiments, UVa (315–400 nm) and vis (400–1050 nm) radiation were used simultaneously. In addition, the SN solutions without TiO₂ and FeCl₃ addition were irradiated using UVa radiation. All of the mixtures were magnetically stirred and had free contact with the air during UVa and vis irradiation. The temperature of the samples was 21 ± 1 °C. Aliquots were removed prior to irradiation and after a specific time followed by centrifugation (30 min, 4000 RPM). These samples were maintained in the dark at room temperature prior to analysis.

2.5. Analytical methodology

The SN concentration in the samples was determined using an HPLC method (YL9100HPLC System: vacuum degasser YL9101, binary pump YL9111, column compartment YL9130, UV/vis detector YL9120 with λ = 272 nm, autosampler SHLA84000, Lab Alliance, column: Vydac C-18, 5 μm, 250 × 2.1 mm). The mobile phase was as follows: (A) H₂O with 0.1% HCOOH, (B) 100% CH₃CN. Gradient elution was applied as follows: 0–4 min, 95:5 (A:B, v/v), 4–8 min, 80:20 (A:B, v/v). The flow rate was 0.6 ml min⁻¹ with a column temperature of 35 °C.

The UV/vis spectra of the SN solutions (0.1 mmol l⁻¹), FeCl₃ (0.1 mmol l⁻¹) and the mixture of each SN solution (0.1 mmol l⁻¹) with FeCl₃ (0.1 mmol l⁻¹) at a pH of 3.0 were determined using a Varian Cary 50 Bio UV–vis spectrophotometer.

2.6. Analysis of results

The radiation energy reaching the sample surface (*Q*_{sur}) in the irradiation time (*t*) was calculated according to the following equation:

$$Q_{\text{sur}} = (I_{\text{UVa}} + I_{\text{vis}}) \times t \quad (1)$$

where *I*_{UVa} and *I*_{vis} are the intensities of UVa and vis irradiation, respectively.

The kinetics of the investigated processes were evaluated as follows:

$$\frac{C_i}{C_0} = f(Q_{\text{sur}}) \quad (2)$$

where *C*₀ is the initial SN concentration in the solution without irradiation and *C*_i is the final SN concentration after the irradiation of the mixtures.

The photocatalytic processes carried out in the presence of TiO₂ or FeCl₃ are believed to be first-order or pseudo first-order reactions [1,3,4,10,18,19]. Therefore, the reaction rate constant (*k*) values are determined from the slope of the linear relationship:

$$\ln \frac{C_0}{C_i} = kQ_{\text{sur}} + b \quad (3)$$

where *b* is the intercept.

To calculate the *k* values in the reactions carried out with FeCl₃, the results were taken into account only when *C*_i/*C*₀ > 0.15.

The concentration of the cationic form of the sulfonamide (SH₂⁺) was calculated according to the mass action law at the actual pH of the solutions [23]:

$$C_{\text{SH}_2^+} = \frac{C_0}{1 + 10^{\text{pH}-\text{pK}_{a1}} + 10^{2\text{pH}-\text{pK}_{a1}-\text{pK}_{a2}}} \quad (4)$$

or

$$C_{\text{SH}_2^+} = \frac{C_{\text{eq}}}{1 + 10^{\text{pH}-\text{pK}_{a1}} + 10^{2\text{pH}-\text{pK}_{a1}-\text{pK}_{a2}}} \quad (5)$$

where *C*_{eq} is an equilibrium SN concentration measured in the solution after the addition of the catalytic system components (i.e., after adsorption but prior to irradiation – the Supplementary material).

Table 3
Experimental results

SNs	Removal (%)		k (m ² MJ ⁻¹)		Vis							
	Adsorption and/or complexation ^a		Photolysis ^b		UVa							
	TiO ₂ (pH ~3)	FeCl ₃ (pH ~3)	TiO ₂ /FeCl ₃ (pH ~3)	Without catalyst	TiO ₂ (natural pH ~4 ± 8)	TiO ₂ (pH ~3)	TiO ₂ with isoprop. (pH ~3)	FeCl ₃ (pH ~3)	TiO ₂ /FeCl ₃ (pH ~3)	TiO ₂ (natural pH ~5 ± 8)	FeCl ₃ (pH ~3)	TiO ₂ /FeCl ₃ (pH ~3)
SAD	0.2 ± 1.8	5.3 ± 1.2	3.5 ± 0.6	3.0 ± 1.2	41.0 ± 0.2	26.0 ± 0.2	0.0 ± 0.5	80.9 ± 0.7	194 ± 19	0.82 ± 0.03	1.25 ± 0.12	1.08 ± 0.09
SCT	-0.8 ± 1.3	4.0 ± 1.3	2.2 ± 0.6	0.0 ± 3.2	37.3 ± 0.8	23.7 ± 0.8	5.6 ± 0.7	62.8 ± 3.0	124 ± 8	0.96 ± 0.16	1.01 ± 0.15	0.62 ± 0.03
STZ	1.0 ± 0.9	5.3 ± 1.5	1.0 ± 0.1	0.1 ± 4.5	40.8 ± 1.7	43.0 ± 0.4	12.4 ± 0.9	81.0 ± 1.4	278 ± 21	0.77 ± 0.10	1.53 ± 0.28	3.23 ± 0.65
SSZ	0.2 ± 2.5	8.5 ± 1.2	9.6 ± 5.2	5.6 ± 3.3	28.5 ± 0.8	29.9 ± 0.9	109 ± 25	61.9 ± 2.7	2556 ± 128	1.22 ± 0.13	1.32 ± 0.07	5.94 ± 0.37
SMX	3.1 ± 2.6	4.0 ± 3.3	2.2 ± 2.0	5.1 ± 3.0	28.1 ± 0.7	28.6 ± 0.8	3.7 ± 0.2	76.7 ± 2.6	90 ± 11	0.66 ± 0.05	1.31 ± 0.08	0.73 ± 0.05
SFZ	1.8 ± 1.0	0.0 ± 0.2	0.9 ± 1.2	0.0 ± 3.2	23.9 ± 0.6 ^c	23.9 ± 0.6	7.1 ± 0.2	69.2 ± 5.6	129 ± 14	0.46 ± 0.04	1.04 ± 0.09	1.17 ± 0.11
SDZ	0.0 ± 1.7	0.9 ± 2.2	1.4 ± 0.1	0.0 ± 1.8	27.5 ± 0.6	16.4 ± 0.3	5.3 ± 0.4	32.7 ± 0.9	155 ± 13	0.65 ± 0.02	0.85 ± 0.07	2.24 ± 0.04
SMR	0.2 ± 0.2	5.2 ± 0.5	61.0 ± 2.8	9.5 ± 3.8	33.4 ± 0.6	30.4 ± 0.4	14.5 ± 0.7	57.5 ± 0.3	170 ± 12	0.79 ± 0.05	0.56 ± 0.18	2.45 ± 0.17
SDM	-1.1 ± 1.6	-1.4 ± 7.0	31.2 ± 5.1	3.6 ± 1.5	47.0 ± 2.2	44.4 ± 1.4	18.5 ± 0.5	72.9 ± 1.9	180 ± 5	1.32 ± 0.12	1.16 ± 0.04	2.79 ± 0.46
SPY	0.6 ± 3.4	1.7 ± 2.4	9.4 ± 3.3	4.8 ± 1.5	42.3 ± 2.6	30.7 ± 1.3	11.2 ± 0.3	59.0 ± 1.8	226 ± 17	1.48 ± 0.09	0.68 ± 0.19	2.02 ± 0.12
SDT	0.3 ± 2.6	1.5 ± 1.2	5.1 ± 4.1	2.4 ± 1.0	31.0 ± 0.6	25.5 ± 0.3	8.0 ± 0.3	52.4 ± 1.0	566 ± 51	1.11 ± 0.27	0.48 ± 0.10	3.54 ± 0.28

All values in the table were calculated as an average of three measurements ± standard deviations.

^a After 30 min stirring in the dark. ^b After 120 min UVA irradiation. ^c At pH 3.15.

The theoretical values of k (k_{cal}) for $I = 0.22 \text{ W m}^{-2}$ (i.e., for the irradiation intensity of the vis lamps in the range of 315–400 nm) (Table 2) were calculated as follows:

$$k_{\text{cal}} = k_{\text{UVA}} \times \frac{0.22}{13.6} \quad (6)$$

where k_{UVA} is the reaction rate constant for processes conducted under UVA irradiation using UVA lamps.

The polarizability values of the studied SNs (Table 1) were obtained from the DrugBank database [24].

2.7. Molecular modelling of sulfonamides

Force field (MMFF94) and Hartree-Fock (HF) methods were used to calculate the molecular properties of SNs (energy minimization and geometry optimization) using the ChemBio3D Ultra version 13.0.2.3021 (PerkinElmer) and Gaussian 09 software packages. The figures showing the 3D structures and atoms charges of all of the studied SNs are included in the Supplementary material. Similar spatial arrangements of atoms in the SN molecules have been previously described [25–28].

3. Results and discussion

3.1. Initial experiments

SNs can undergo changes in the aqueous solutions due to different physicochemical and biochemical processes (e.g., adsorption, hydrolysis, photolysis or biodegradation). The processes that occur simultaneously during photocatalytic degradation may lead to incorrect assessment of the results. To eliminate the potential errors caused by these processes, we initially determined the decrease in the SN concentration ($C_0 = 0.1 \text{ mmol l}^{-1}$) caused by:

- acidic hydrolysis (in $0.1 \text{ mol l}^{-1} \text{ HCl}$),
- photolysis, and
- adsorption – after the addition of TiO_2 (0.05 g) and FeCl_3 (1.0 mmol l^{-1}) in the dark.

Under the experimental conditions, SCT was the only SN that hydrolyzed, and its half-life was 28 h. Other SNs were nearly stable and did not decompose due to hydrolysis within 21 days. The results (without hydrolysis) are shown in Table 3. A decrease in the concentrations of the SN solutions caused by photolysis (initiated by UVA radiation) was negligible under the experimental conditions (Table 3). This result indicates that the previously mentioned processes have no significant affect on the k determination.

A decrease in the concentration of each SN solution was not significant in the presence of TiO_2 in the dark. In the $\text{TiO}_2/\text{FeCl}_3$ mixture, a significant decrease in the concentrations (>10%) was observed in the SMR and SDM samples without irradiation (Table 3). In contrast to the other SNs, SMR and SDM form a bond with FeCl_3 , which was identified using a spectrophotometric method. Their spectra with FeCl_3 were different from those calculated based on the additivity of absorbances (Fig. 2). However, the presence of SN complexes with FeCl_3 was not confirmed by HPLC analysis (Table 3) due to the weakness of this bond. The formation of complex compounds by SNS with transition metal ions (Co^{2+} , Ni^{2+}) has been previously observed by Mondelli et al. and others [27,28]. A decrease in the SMR and SDM concentrations in the supernatant may be due to adsorption of the complexes onto the TiO_2 particles. An adsorption of SSZ and SPY onto the $\text{TiO}_2/\text{FeCl}_3$ mixture was significantly lower (~9%).

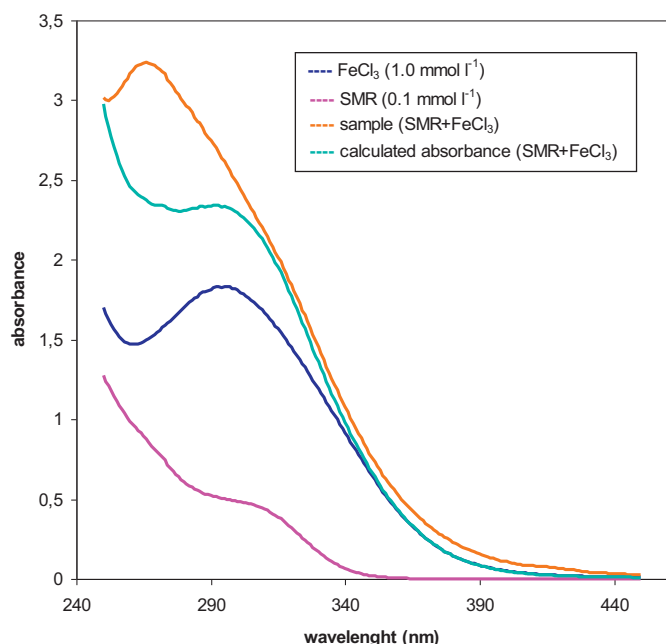


Fig. 2. Comparison of the UV-vis spectra of SMR and the FeCl_3 solutions with the calculated spectrum and the actual spectrum of a solution containing SMR and FeCl_3 .

3.2. Assessment of the dynamics of photocatalytic degradation during UVA irradiation

The dynamics of photocatalytic degradation of the eleven sulfonamides (0.1 mmol l^{-1}) were studied after UVA irradiation in the presence of TiO_2 (0.5 g l^{-1}) or/and FeCl_3 (1.0 mmol l^{-1}). The photocatalytic reactions carried out in the presence of FeCl_3 operate only in a narrow pH range of ~ 3 . According to the literature data and results from our previous studies, the photocatalytic reaction rates in the presence of the $\text{TiO}_2/\text{FeCl}_3$ mixture are typically the fastest at a pH ~ 3 . However, these reactions are inhibited at pH > 3.5 – 4 regardless of the substrate type in the photocatalytic process [10,11,14–19]. This result is most likely related to the presence of photoactive $\text{Fe}(\text{OH})^{2+}$ ions because their concentration substantially decreased due to hydrolysis in the aqueous solutions at a pH greater than 3.5 [29]. Therefore, if necessary, the pH of the samples was corrected to 3 prior to irradiation. The samples containing only TiO_2 as the catalyst were irradiated at their original pH and at a pH of 3. The original pH values of the SN solutions with TiO_2 are listed in Table 1. Fig. 3 shows the dynamics of photocatalytic degradation during UVA irradiation of samples containing the studied catalysts and SAD as an example. In the upper right corner of Fig. 3, $\ln C_0/C_i = f(Q_{\text{sur}})$ is shown. The photocatalytic reaction was inhibited at $C_i/C_0 < 0.15$ during UVA irradiation of the samples containing the $\text{TiO}_2/\text{FeCl}_3$ mixture. Comparable changes were observed for all of the studied SNs, which may be due to the reduction of Fe^{3+} to Fe^{2+} [9,10,15,16,18].

The experimental results are shown in Table 3. The k values were calculated based on the method described in Section 2.6.

All of the SNs used in the experiment underwent photocatalytic degradation after UVA irradiation. In most cases, the reaction rate in the presence of TiO_2 only varied due to the change in pH from the original value to the corrected pH value. This value affects the charge on the TiO_2 surface and the form (i.e., cationic, neutral or anionic) of the substrate molecule. The same charge on the substrate and catalyst particles is not beneficial to adsorption and the photocatalytic reaction rate. The point of zero charge (pH_{pzc}) for TiO_2 -P25 is approximately 6.3 [30,31], which indicates that in most experiments at the original pH (except SAD, SSZ and SPY), the

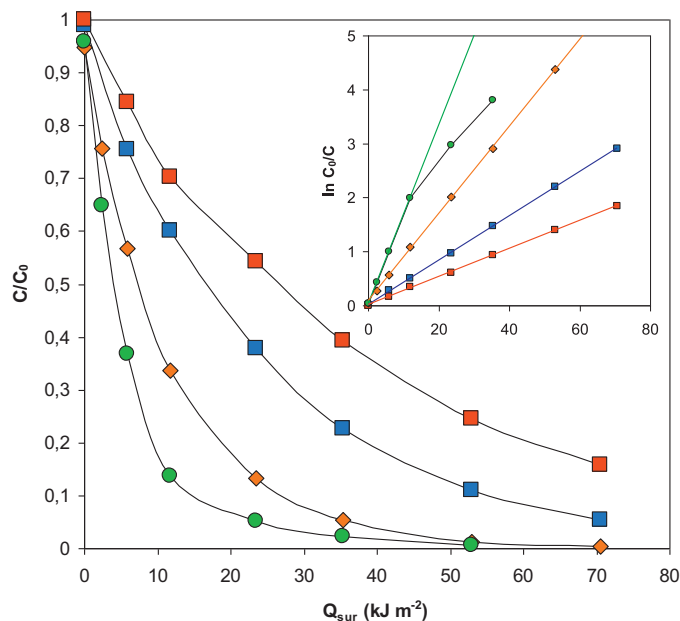


Fig. 3. Photodegradation of SAD during UVA irradiation in the presence of TiO_2 (at natural pH 6), TiO_2 (at pH 3), FeCl_3 (at pH 3) and $\text{TiO}_2/\text{FeCl}_3$ (at pH 3).

catalyst particles possess a positive charge, whereas the substrates molecules were neutral [23,30]. A decrease in the pH to 3 resulted in a simultaneous decrease in the concentrations of neutral substrate particles as well as the observed decrease in the reaction rate (for all SNs except STZ). The pH effect on the photocatalytic degradation rate of SNs (having different pK_a values) in the presence of TiO_2 has been described in detail by Yang et al. [30].

The $\text{TiO}_2/\text{FeCl}_3$ mixture exhibited the highest activity among the studied catalysts, and SSZ exhibited a high rate of photodegradation. Under these conditions, SSZ was completely decomposed (in 100%) after 120 s of UVA irradiation. The other SNs were $\sim 15\%$ (SMX) to $\sim 40\%$ (SDT) decomposed under the same experimental conditions (i.e., after 120 s of UVA irradiation using the $\text{TiO}_2/\text{FeCl}_3$ mixture). The SMR concentration was less than 65% of its initial concentration after 120 min of UVA irradiation in the presence of $\text{TiO}_2/\text{FeCl}_3$, which may be due to the adsorption of SMR rather than the photocatalytic degradation process (Section 3.1).

3.3. Assessment of the dynamics of the photocatalytic degradation under vis irradiation

The SN solutions were irradiated with visible light in the presence of the same photocatalytic systems described in Section 3.2. These solutions, which only contained TiO_2 as the catalyst, were irradiated at the original pH value. The results are shown in Table 3. The results of the photocatalytic degradation with TiO_2 at a pH of 3 were not significant for this study and are not included in Table 3.

In the experiments, a cut-off filter, which absorb radiation $< 400 \text{ nm}$, was not used, which resulted in a significantly simpler procedure.

The visible light source emitted approximately 0.5% UVA radiation (Table 2). The k_{cal} values were determined to assess the effect of vis light on the photocatalytic process. These values were calculated for reactions carried out at an irradiation intensity corresponding to the UVA irradiation emitted by the vis lamps (Eq. (4)). In the determined range, the photocatalytic reaction rate was directly proportional to the irradiation intensity absorbed by the photocatalyst [1–4,32]. This fact has been taken into account in the calculations. The detailed data are shown in Section 2.6. The mean

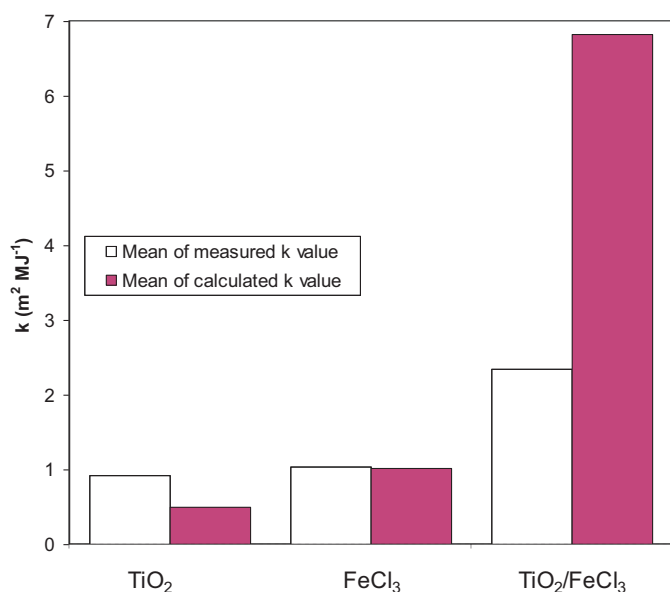


Fig. 4. Mean values of k and k_{cal} calculated for the photocatalytic degradation of all of the SNs using vis lamps (Table 2).

values for k_{cal} and k , which were calculated for the photocatalytic reactions carried out with vis lamps, are shown in Fig. 4.

TiO₂ and FeCl₃ only exhibit low catalytic activity for the employed light source (vis lamps). This activity was most likely due to only UVa radiation because the k and k_{cal} values were similar. Therefore, FeCl₃ and complex compounds with the Fe³⁺ ions that were formed at the a pH of 3 were not active at a wavelength >400 nm. In contrast, the photocatalytic activity of the TiO₂/FeCl₃ mixture was much lower than expected ($k \ll k_{cal}$). These results suggest that both TiO₂ and FeCl₃ use the radiation energy at wavelengths close to 400 nm to a greater extent than the TiO₂/FeCl₃ mixture. However, the most important conclusion is that the TiO₂/FeCl₃ mixture does not catalyze SN degradation at a wavelength >400 nm.

3.4. Mechanism of the photocatalytic process carried out in the presence of the TiO₂/FeCl₃ mixture

As previously mentioned, the most important aim of this study was to explain the high activity of the TiO₂/FeCl₃ mixture during the photocatalytic degradation of SNs.

The k value for photocatalytic SN degradation (except SMX) carried out in the TiO₂/FeCl₃ mixture ranged from 1.39 to 27.8 times higher than the algebraic sum of the k values determined separately for the reactions carried out with TiO₂ (at pH 3) and FeCl₃ (Table 3). A similar effect was previously described by Měšťánková et al. [11] and Nahar et al. [15]. This result indicates that the higher photocatalytic degradation rate of the SNs in the TiO₂/FeCl₃ mixture was not due to an increase in the amount of HO• radicals simultaneously generated on the TiO₂ surface during the irradiation of the Fe(OH)²⁺ ion.

There was no correlation between the photocatalytic degradation rate of the studied SNs and adsorption/complexation, photolysis and the rate of acidic hydrolysis under the experimental conditions (Table 4). Based on the experiments performed (Section 3.3), the higher photocatalytic degradation rate of SNs in the TiO₂/FeCl₃ mixture was not due to an increase in the spectral range that activates the photocatalytic process.

This result was confirmed by the experimental results reported by Zhang et al. [20] where Fe³⁺ ions were not incorporated in the crystal lattice of TiO₂. Therefore, these ions did not reduce the band

Table 4

Correlations between the k values of photocatalytic SNs degradation and their susceptibility to adsorption, complexation, photolysis (at pH 3), acid hydrolysis and polarizability

	R ² values		
	TiO ₂	FeCl ₃	TiO ₂ /FeCl ₃
Adsorption and/or complexation degree	0.0134	0.0563	0.0026 (0.4305) ^b
Photolysis degree ^a	0.0452	0.0011	0.0649
Acidic hydrolysis rate	0.0591	0.0090	0.0035
Polarizability	0.0749	0.0587	0.0309

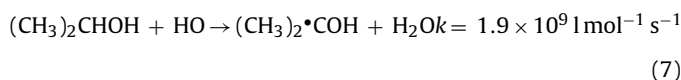
^a After 120 min UVa irradiation. ^b Without SMR and SDM.

gap. However, according to Yalcin et al. [13], it is possible to excite the Fe-doped TiO₂ surface using low energy radiation.

The high activity of the TiO₂/FeCl₃ mixture was not caused by the formation of complex photoactive compounds of SNs with Fe³⁺.

Fe³⁺ ions and their hydrolysis products can adsorb onto the surface of TiO₂ particles [15,20]. Therefore, the rate-limiting processes of the photocatalytic photodegradation of SNs should occur on the catalyst surface. For the TiO₂/FeCl₃ mixture, the pH_{pzc} was approximately 6.8 (under experimental conditions, our non published data), and for TiO₂, pH_{pzc} was only 6.3. This result indicates that the particles of the photocatalyst suspension possess positive charges at a pH ~3. Therefore, the adsorption of cationic substrates on their surface should be difficult. A decrease in the adsorption and the photocatalytic reaction rate should occur when the pH decreases. This correlation was only observed in the presence of TiO₂ only. However, in the presence of the TiO₂/FeCl₃ mixture, this correlation appears to be negligible. The decrease in the SN concentration prior to irradiation in the presence of TiO₂/FeCl₃ was 11.6% on average, which was higher than that in the presence of only TiO₂ (0.5%) and FeCl₃ (3.2%). Similar results have been reported by Zhang et al. [20]. This phenomenon is not correlated to the polarizability (Table 1), which is the ability to create dipoles by the studied SNs. Therefore, we assume that weak electrostatic interactions between organic substrates and TiO₂/FeCl₃ are feasible. The formation of these interactions has also been suggested by other authors [17,20,33,34].

According to many studies, the photocatalytic degradation process of organic substrates is initiated by hydroxyl radicals (HO•) [2–5,19,20,30,31]. Isopropanol has been used as a radical scavenger to determine the role of HO• during the photocatalytic degradation of organic compounds. Highly active HO• radicals, which are generated on the TiO₂ surface, react with isopropanol to form relatively inert isopropyl radicals [35]:



The mean photodegradation rate of the SNs (except SSZ) decreased by approximately 90% after the addition of excess isopropanol (0.1 mol l⁻¹) to the solutions containing TiO₂. However, the mean photodegradation rate of all of the SNs in the TiO₂/FeCl₃ mixture with isopropanol only decreased by 40% (Table 3). These results indicate that the participation of free radicals including HO• radicals in the photocatalytic degradation of SNs in the presence of the TiO₂/FeCl₃ mixture was significantly lower than that in the TiO₂ suspension.

In addition, based on these results, we assume that the most important factor affecting the degradation rate of SNs in the TiO₂/FeCl₃ mixture was the hole (h⁺) generating rate and electron transfer from a substrate particle to h⁺ by iron ion(s) adsorbed on the TiO₂ surface. Simultaneously, a process initiated by HO• radicals (as determined in our previous studies) [19] also occurs. However, this process has a smaller effect on the degradation rate of SNs.

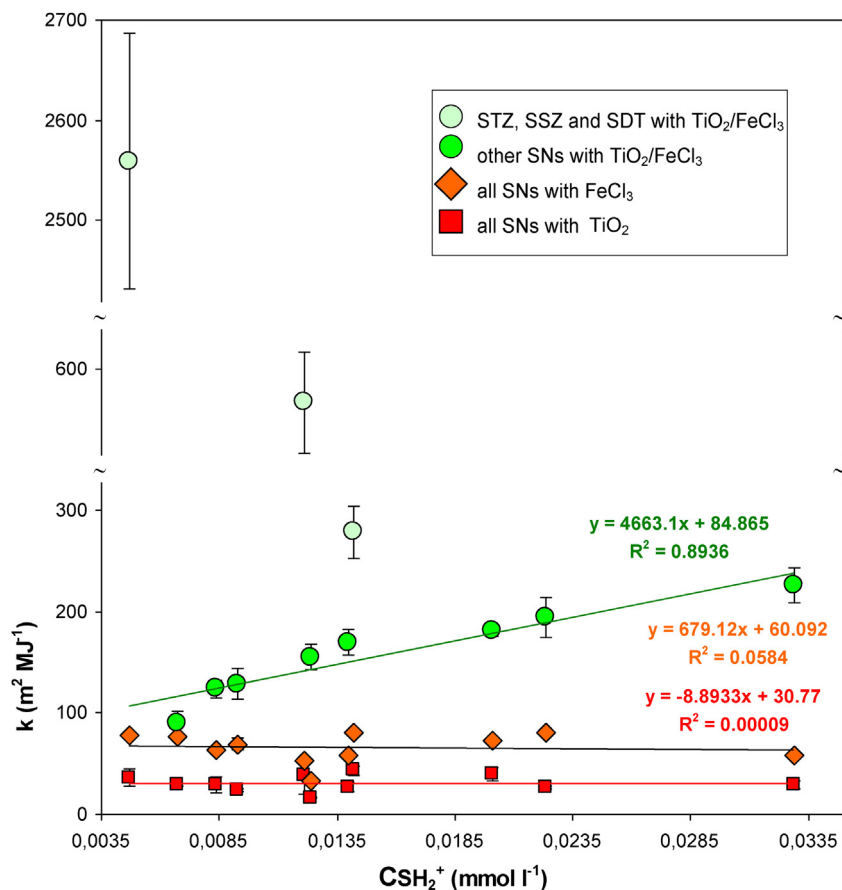


Fig. 5. Effect of the concentration of the cationic form of SN (CSH_2^+) on the photocatalytic degradation rate during UVA irradiation at a pH of 3; $n = 3$.

In the presence of the $\text{TiO}_2/\text{FeCl}_3$ mixture, Fe^{3+} ions may react with photoexcited electrons (e^-) and, simultaneously undergo reduction:



The results from our previous experiments confirm the presence of Fe^{2+} ions in solutions obtained after photocatalytic degradation of SAD [18]. A significant increase in the photocatalytic process rates was achieved by preventing recombination between h^+ and e^- [2–5,20,36], which may also be important in the current study. However, reaction (8) is competitive with the generation of HO^\bullet from dissolved oxygen [9].

According to the Langmuir Hinshelwood theory, the possibility that the substrate molecules bind to the surface of heterogeneous catalysts has a significant influence on the photocatalytic reaction rate. In the solutions at a pH of 3, SNs are considered to be neutral molecules and SH_2^+ cations [23]. There is a positive linear correlation between the SH_2^+ concentration in 8 out of 11 SNs (except SSZ, SDT and STZ) and the k values of the reactions carried out with the $\text{TiO}_2/\text{FeCl}_3$ mixture (Fig. 5). However, there is no such correlation for the reactions carried out with only TiO_2 and FeCl_3 . Analogous results were obtained after analysis of the relationship between k and the SH_2^+ concentration (in the Supplementary material). The SH_2^+ concentration was calculated based on the equilibrium SN concentration, which was measured in the solution after the addition of the catalytic components and stirring in the dark (Section 2.6). These observations indicate that the presence of the SH_2^+ ion in irradiated samples has a significant influence on the reaction rate in the $\text{TiO}_2/\text{FeCl}_3$ mixture. Based on these facts, this ion should adsorb on the catalyst surface. Fig. 6 shows the proposed cationic binding of SNs with TiO_2 particles in the presence of Fe^{3+} ions. In

both the anatase and rutile structure, the Ti^{4+} ion is surrounded by six O^{2-} ions [3]. Therefore, the formation of electrostatic interactions between the surface oxygen anions and a substrate with positive charge (e.g., hydrogen ion (H^+) in the amine group of SN) is possible. In addition, the amino group with a positive charge can facilitate the appropriate spatial orientation of the SN molecule to the catalyst surface.

The photocatalytic degradation rate of SDT, STZ and SSZ was higher than expected, which may be due to favorable steric effects. Fig. 6 shows the spatial arrangement of the atoms in two SNs. The horizontal position of the heterocyclic ring (Fig. 6a) (e.g., in SDT, STZ, SFZ and SSZ) increases the possibility of coordination of the SNs with the catalyst surface. The study by Mondelli et al. [27,28] confirms our hypothesis based on their description of the influence of the spatial orientation of the heterocyclic rings in the SNs on the formation of coordinative bonds with the transition metal cations. The 3D structures of the studied SNs are included in the Supplementary material. Regardless of the calculation method (MMFF94 or HF), the results were very similar with regards to the possibility of forming bonds with the $\text{TiO}_2/\text{Fe}^{3+}$ system.

In a solution at a pH of 3, the SH_2^+ ion concentration was closely related to the K_{a1} value of the SNs. Therefore, the correlation between the k and K_a values was also investigated. A high negative correlation ($R^2 = 0.9915$) was observed for 8 SNs in the $\text{TiO}_2/\text{Fe}^{3+}$ mixture, which indicates that less polar SNs or those with heterocyclic groups with a low electron affinity could easily form bonds with the Fe^{3+} ions adsorbed on the TiO_2 surface. Due to the positive charge of the surface of the $\text{TiO}_2/\text{FeCl}_3$ catalyst (at pH 3), the SH molecules could be involved in these interactions because their concentration was higher by 2 to more than 20 times than that of the SH_2^+ ions under this pH condition. However, in our opinion,

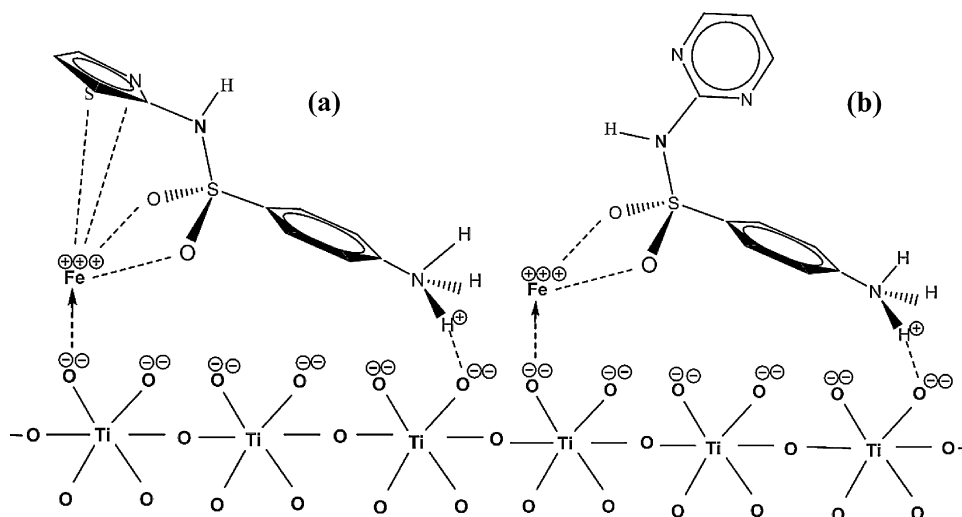


Fig. 6. Possible interaction of SNs with $\text{TiO}_2/\text{FeCl}_3$: (a) spatial configuration of atoms in STZ, (similar configurations have SSZ and SFZ molecules – Supplementary materials); (b) spatial configuration of atoms in SDZ (similar configurations have SMX, SMR, SDM, SPY and SDT molecules – Supplementary materials); Interactions between Fe^{3+} ions and oxygen atoms of the sulfone group, nitrogen atom of the heterocyclic ring and oxygen atom of the methoxy group is also possible for SDT. The water molecules were omitted for clarity.

this mechanism is not likely due to the complete inhibition of the photocatalytic degradation of SNs in the presence of $\text{TiO}_2/\text{FeCl}_3$ at $\text{pH} > 3.5$ [10,11,19].

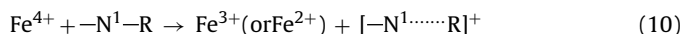
The particularly high photodegradation rate of SSZ in the presence of $\text{TiO}_2/\text{FeCl}_3$ cannot be explained only by steric effects. This reaction rate was approximately 85 times higher than the reaction rate of SSZ with TiO_2 at a pH of 3 and more than 12 times higher than the mean reaction rate of other SNs with $\text{TiO}_2/\text{FeCl}_3$. Photolysis, biodegradation, hydrolysis or stable binding to the components of the photocatalytic system had no effect on the photocatalytic degradation rate of SSZ. A photoactive complex compound consisting of SSZ with Fe^{3+} was not formed. In contrast to other studied SNs, the SSZ degradation rate increased after isopropanol addition to the reaction medium containing only TiO_2 . Another characteristic of SSZ is the formation of SAD, which is a photodegradation product, in stoichiometric amounts. In turn, the degradation products of other SNs included sulfanilic acid, aromatic amines and benzoic acid [19,37]. These results indicate that the first stage of SSZ degradation is cleavage of the $\text{N}^1\text{—R}$ bond, which is most likely much weaker than those in other SNs. In the SSZ molecule, the R-group is characterized by the highest electrons affinity (for SSZ, the $\text{pK}_{\text{a}1}$ and $\text{pK}_{\text{a}2}$ values were the lowest) and the lowest charge on the carbon attached to N^1 (Table 1). However, the charge calculated using the HF method for the carbon atom bonded to the amide nitrogen (C12) was significantly different from the result obtained using the MMFF94 method (the Supplementary material). In addition, the results calculated using the HF method are inconsistent with the experimental data (e.g., they do not correspond with the pK_{a} values of SNs).

Therefore, the sulfonamide group is less susceptible to protonation, and SSZ is resistant to acidic hydrolysis [38]. Even a small energy destabilization of the SSZ molecule can result in cleavage of the $\text{N}^1\text{—R}$ bond. Therefore, the isopropyl radical energy is sufficient to initiate SSZ degradation in the presence of TiO_2 and isopropanol. The very high rate of SSZ degradation during UVA irradiation of solutions containing $\text{TiO}_2/\text{FeCl}_3$ indicates that the radiation energy was not transferred in this SN via free radicals (HO^\bullet or O_2^-). Due to the high activity of these radicals, they may be involved in parallel processes (i.e., propagation and termination) with the substances available in the reaction medium. Therefore, the energy transferred by the participation of free radicals would undergo dispersion. One of the possible ways to initiate the degradation process involves

the transfer of h^+ energy to SSZ via the Fe^{3+} ion. According to this mechanism, the Fe^{3+} ion would initially act as an electron donor:



and then as an electron acceptor:



A stable Fe^{4+} ion does not form during the photocatalytic process due to the high potential of the $\text{Fe}^{4+}/\text{Fe}^{3+}$ system. However, short-lived Fe ions without 4 electrons may be locally generated during the electron transfer process from the substrate to h^+ . This phenomenon has been described by Menéndez-Flores et al. [14]. A similar energy transfer path occurs in aqueous medium in the peroxidase cycle of myoglobin [39]. The quantity of energy transferred in this way may be insufficient to initiate the reaction with H_2O or other SNs but it may be sufficient to destabilize the weak $\text{N}^1\text{—R}$ bond in the SSZ molecule. However, this hypothesis does not explain why the reaction rate decreased by approximately 40% in the presence of isopropanol.

As previously mentioned, in addition to the previously discussed methods of photocatalytic SN degradation in the presence of $\text{TiO}_2/\text{FeCl}_3$, the parallel processes initiated by HO^\bullet also occurs. The explanation of the mechanism of the high susceptibility of SSZ to photocatalytic degradation may be important in practice. There is a high probability that the characteristic features of the SSZ molecule determine its high susceptibility to degradation, which could be used during drug design. Widespread use of such a designed antibiotics in animal husbandry would facilitate their selective elimination from wastewater during the photocatalytic process as a pre-treatment step. In addition, wastewater disinfection and decomposition of potentially dangerous genes that exhibit antibiotic resistance will simultaneously occur during this process. The high rate of the photocatalytic process and the use of UV radiation, which is part of natural sunlight, can guarantee that the overall costs of the construction of a pilot scale installation may be possible.

4. Conclusion

Under UVA irradiation, the addition of FeCl_3 to a commercial catalyst (i.e., $\text{TiO}_2\text{—P25}$) significantly increased the photocatalytic activity. The SN photodegradation rates were directly proportional to the concentration of the cationic form of the substrate. However,

no correlation with the adsorption/complexation, polarizability, photolysis degrees or acidic hydrolysis rate was observed. The photocatalytic SN degradation in the presence of $\text{TiO}_2/\text{FeCl}_3$ primarily proceeded via hole oxidation and, to a lesser extent, by reactions with hydroxyl radicals. The formation of electrostatic interactions between the surface oxygen anions, Fe^{3+} ions and the substrate, which possesses a positive charge and lone pairs of electrons, plays a major role in this process. The higher photodegradation rate of SDT, STZ and SSZ may be due to a favourable steric effect and the formation of a greater number of bonds between Fe^{3+} ions and lone pairs of electron on SNs. The very high rate of SSZ photodegradation may be due to facile cleavage of bonds between the nitrogen atom in the amide group and the carbon atom in the heterocyclic ring. The $\text{TiO}_2/\text{FeCl}_3$ mixture was not active during SNs photodegradation initiated by vis radiation.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2015.02.025>.

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